

# PATENT SPECIFICATION

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## (54) A MARINE STRUCTURE HAVING A SURFACE COATING FOR THE PREVENTION OF ACCUMULATION OF MARINE ORGANISMS

(71) I, KARL KRISTIAN KOBS KRØYER, a subject of the King of Denmark of Vestre Kongevej 80, 8260 Viby J., Denmark, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a marine structure such as a ship hull and a buoy having surfaces intended for immersion in sea water and comprising a surface coating having antifouling properties and useful for preventing the accumulation of organisms on said surfaces.

The protection and maintenance of surfaces of structures in contact with sea water such as ship's hulls present difficulties because such surfaces normally are fouled by organisms such as green and brown algae, barnacles, tube worms, serpula, oysters, ascidia, bryozoa etc. Such deposits are also a nuisance on ship's hulls where they add to the weight and increase frictional resistance leading to higher fuel costs, slower speeds and increased engine wear unless they are frequently removed or their growth or accumulation are prevented.

Antifouling paint coats are been used on ship's hulls to prevent the growth and accumulation of marine organisms. However, it has been found that it is unnecessary to prevent the settling of fouling organisms entirely and that an antifouling coat is effective if tight adherence of the organisms is being prevented so that these organisms are washed away when the ship is sailing.

Some antifouling coatings have been developed to reduce the adherence between marine organisms and ship's hulls. As examples of such coatings polytetrafluoroethylene and silicone resin coatings may be mentioned.

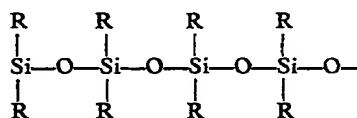
When applying silicone resin coatings onto a ship's hull a silicone compound which may be condensed to the desired silicone resin is dissolved in a volatile solvent and the solution is applied to the surface to be coated and per-

mitted to dry. The coating thus formed is then baked to cause condensation polymerisation of the silicone to form the silicone resin. The final coating has a hard and smooth surface.

The invention is based on the discovery that a more efficient antifouling effect can be obtained and that the use of volatile solvents for the application of the coating can be avoided.

The invention consists of a marine structure part at least of the outer surface of which is intended to be immersed in sea water characterised in that there is provided upon said surface a coating of one or more layers, the or the outermost one of which comprises a vulcanised silicone rubber which is substantially free from toxic compounds.

Silicone rubbers constitute a class of rubber-like polymers with special physical and chemical properties. Chemically they are specially prepared polymers of purified disubstituted siloxane in which the reaction is controlled to give linear chains of several thousand units:



where R represents substituted or unsubstituted alkyl, aryl or vinyl groups.

Although the polymer is saturated it can be vulcanised by heating with a free-radical reagent such as benzoyl peroxide. The free radicals derived from benzoyl peroxide probably abstracts hydrogen atoms from the polymer molecules. The free valences of the polymer molecules then lead to crosslinks which results in a vulcanized product.

An outstanding characteristic of silicone rubbers is their very broad useful temperature range (—73°C to 260°C). In this range flexibility, resilience and tensile strength are retained to an amazing degree. Resistance to weathering and ozone is also excellent.

Special types of silicone rubbers are avail-

able which can be cured at room temperature. Such silicone rubbers (room temperature vulcanizing rubbers, RTV) are particularly preferred because of the ease of application of such products.

Heat-curing types of silicone rubbers are made up of gums, fillers, additives and catalysts. They are commercially available as gums, reinforced gums (gum and a portion of a filler), uncatalized compounds, dispersions and catalized compounds. The last mentioned are compositions which are ready for use.

The uncured rubber mixtures range from a tough putty to a hard deformable plastic in consistency. The putty-like mass is particularly preferred for application on ship's hulls by means of brushes, scrapers etc.

The room temperature vulcanizing silicone rubbers comprise silicone fluids with silanol end groups. Fillers are used in much the same way as in heat cured rubber, but must be compatible with the curing agent. For some types of room temperature vulcanizing rubbers the polymer is mixed with the filler and ethylsilicate. A catalyst such as dibutyltin dilaurate is stirred in just before using the material. Polymerization begins immediately with elimination of ethyl alcohol. The pot life and the work life depend on several factors but is generally on the order of a few hours at room temperature.

Another type of room temperature vulcanizing rubbers is made by mixing polymer, filler, cross-linking agent and curing catalyst and packaging the mixture to protect it from moisture. Contact with air brings about reactions which cure the polymer.

The cured silicone rubber coating is softer than a silicone resin layer. Surprisingly, it has been found that the fouling is less serious on relatively soft surfaces than on hard surfaces and that the removal of organisms clinging to the coated surface require less energy if the coating consists of relatively soft silicone rubber than of a hard smooth layer of silicone resin. Due to the fact that silicone rubbers can be applied without the use of solvents which

may be inflammable and toxic, a serious drawback of the prior art technique is also eliminated.

Prior to the application of the silicone rubber coating the surface is preferably cleaned, for example by sand blasting. Subsequently, an anti-corrosive coat is applied and on top thereof a layer of an adhesive promoter. Finally, the silicone layer is applied on top of the adhesive-promoting layer.

In order to compare the antifouling coating of the invention with the prior art antifouling coatings, the following tests were performed.

Metal panels provided with different coatings were installed on a float at Florida Marine Research Laboratories, Daytona Beach, Florida, and were kept submerged in sea water for thirty days. The panels were then removed for water jet testing to determine the removal of the organisms adhering to the surfaces when subjected to the effect of different water jets. The panels were subjected to the effect of water jets from three jet nozzles having a diameter of 4, 2,5 and 0,5 mm respectively at pressures ranging from 0 to 25 atmospheres. After being subjected to the effect of said water jets the panels were inspected and the removal of fouling visually evaluated according to a scale from 0 to 10. If there was no effect of a given water jet the panel was graded 10. If all algae "grass" lost adhesion it was graded 0.

To show the comparative effectiveness of each jet the panels were divided vertically into three sections. The left section of the panel was subjected to a jet from the 4 mm nozzle, the centre portion to the jet from the 2,5 mm nozzle and the right portion to the jet from the 0,5 mm nozzle. The surface not under test was protected by covering it with neoprene rubber.

The effect of the jets on hard fouling was recorded at each reading as "no effect" (NEHF) or "some effect" (SHF).

The characteristics of the panels inspected will appear from the following table:

TABLE 1

Panel No.	Support		Priming	Coating
	Type	Size		
1	Aluminum	300 × 300 × 2 mm	Etching	Polytetrafluoroethylene, 20—25 $\mu$ m
2	Aluminum	300 × 300 × 2 mm	Electrolytical oxidation	Owen-cured silicone lacquer
3	Aluminum	300 × 300 × 2 mm	"	Open air dried silicone lacquer
4	Iron	300 × 300 × 2 mm	Two layers of rust-inhibiting agent (Hempel Platin Primer 1002)	1.5 mm thick coating of silicone rubber (Silastic RTV E, supplied by Dow-Corning Corp.)

The inspection data will appear from the following table.

Panel No.	Pressure, atm.	4 mm jet		2,5 mm jet		0,5 mm jet	
		Algae*) adherence	Hard fouling**)	Algae*) adherence	Hard fouling**)	Algae*) adherence	Hard fouling**)
1	3.46	9	NEHF	7	SHF	7	SHF
	10.38	8	„	6	NEHF	5	„
	17.31	7	„	4	SHF	2	„
	24.24	5	SHF	1	SHF	2	„
2	3.46	10	NEHF	9	SHF	9	SHF
	10.38	10	„	9	NEHF	9	NEHF
	17.31	10	„	8	„	9	SHF
	24.24	9	„	7	„	8	NEHF
3	3.46	9	NEHF	8	NEHF	8	NEHF
	10.38	9	„	9	„	6	„
	17.31	9	„	5	„	5	„
	24.24	5	„	3	„	3	„
4	3.46	9	NEHF	8	SHF	8	SHF
	10.38	9	„	7	NEHF	5	NEHF
	17.31	9	„	6	SHF	3	all removed
	24.24	8	„	3	all removed	0	all removed

\*) Evaluated according to a scale ranging from 0 to 10, 0 = total effect, 10 = no effect.

\*\*\*) NEHF = No effect on hard fouling.

SHF = Some hard fouling loses adherence.

- As will appear from the above data the adhesion of algae on the silicone rubber coated panel is less severe than on panels coated with silicone lacquer and polytetrafluoroethylene.
- 5 Furthermore, it appears from table 2 that only on the silicone rubber coatings the hard fouling can be totally removed with the strongest water jet.
- 10 In order to ensure that the antifouling effect is not completely lost if the silicone rubber coating is removed from the projected surface, e.g. due to ageing or accidental contact with hard objects, it is preferably applied on top of a commonly used antifouling coating containing toxic compounds which are gradually leached out from said coating. Thus, it may be desirable to apply an antifouling coating containing toxic metal oxides in a copolymer of vinylacetate and vinylchloride on top of an anti-corrosive coating and to apply a primer on top of said antifouling coating. Finally, the silicone rubber layer is applied on top of the primer.
- 20
- Example
- 25 Four coating systems according to the invention applied on steel panels were investigated by exposing the test panels to the influence of sea water containing algae and barnacles.
- The adhesion of the fouling was determined by visual inspection.
- 30 The panel system used and the results obtained will appear from the following table.

TABLE 3

Panel No.	Paint System			Film thickness, microns			Fouling*)			
	Anticorrosive coating	Sealing coating	Antifouling coating	Anti-corrosive coating	Sealing coating	Anti-fouling coating	Mounting of panels during 56 days exposure	Algae	Barnacles	Others
A-1	Zincsilicate paint (Galvosil 1561)	Polyvinyl-butylal (Wash primer 1520)	Silicone rubber (Silastomer 9161)	80	15	135	Vertical depth 10 cm	-	-	-
A-2										
A-3	"	"	"	80	15	135	Horizontal depth 1 m	±	±	±
A-4										
B-1	Zincsilicate paint (Galvosil 1570)	"	"	80	15	105	Vertical depth 10 cm)	-	-	-
B-2										
B-3	"	"	"	80	15	105	Horizontal depth 1 m	±	±	±
B-4										
C-1	Zinc silicate paint (Galvosil 1561)	Adhesive promoter (Primer MS 2402)	"	80	10	110	Vertical depth 10 cm	-	-	-
C-2										
C-3	"	"	"	80	10	110	Horizontal depth 1 m	±	±	±
C-4										
D-1	Zincsilicate paint (Galvosil 1570)	"	"	80	10	110	Vertical depth 10 cm	-	-	-
D-2										
D-3	"	"	"	80	10	110	Horizontal depth 1 m	±	±	±
D-4										

\*) - no fouling, + fouling, firmly attached, ± fouling, not firmly attached, ++ serious fouling.

As will appear from table 3 no fouling or a fouling which is not firmly attached occurred by use of the four paint systems.

- 5 The systems A, B and C showed insufficient adherence after the exposure period and were not subjected to further tests. System D was subjected to a rotor test to determine the adherence of fouling when the sample is moved relative to the water in which the sample is
- 10 immersed. The sample was rotor tested at a speed of 30 knots during 24 hours. During this test the fouling from the panels D was washed off immediately. The coating system withstood the turbulent water flow. The rotor
- 15 test apparatus is described in the article: "Testing and Investigation of Ship Bottom Paints (Journal Oil. Col. Chem. Assoc. 52, p. 141—157 (1969)).

#### WHAT I CLAIM IS:—

- 20 1. A marine structure part at least of the outer surface of which is intended to be immersed in sea water characterised in that there is provided upon said surface a coating of one or more layers, the or the outermost one of
- 25 which comprises a vulcanised silicone rubber which is substantially free from toxic compounds.
2. A marine structure according to claim 1 characterized in that the silicone rubber is
- 30 a room temperature vulcanizing rubber.

3. A marine structure according to claim 1 characterized in that it also comprises an anticorrosive subcoating.

4. A marine structure according to claim 3, characterized in that it further comprises an adhesive promoting coating located between said anticorrosive coating and said silicone rubber coating.

5. A marine structure as claimed in claim 3 characterized in that it further comprises a protective coating containing toxic metal compounds and a primer coating disposed between said anticorrosive subcoating and said silicone rubber layer.

6. A marine structure part at least of the outer surface of which is intended to be immersed in sea water substantially as herein described with reference to the example.

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